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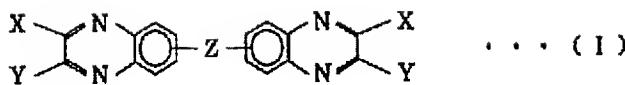
25 (54) [Title of the Invention] Organic Electroluminescence Element

(57) [Abstract]

[Object] To develop an organic electroluminescence element achieving a high accuracy, a high luminous efficiency, and a longer lifetime.

[Constitution]

30 [Chemical formula 1]

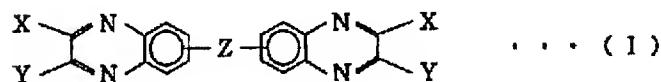


An organic electroluminescence element which contains a quinoxaline compound shown by the general formula (I) (symbols in the formula are given in the specification).

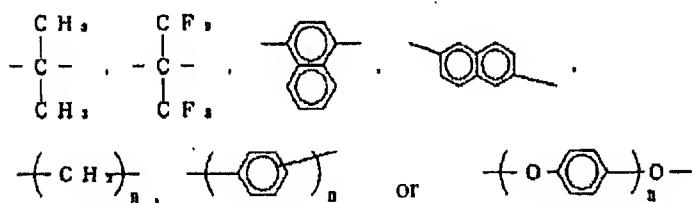
5 [Scope of Claims]

[Claim 1]

[Chemical Formula 1]



[Chemical Formula 2]



An organic electroluminescence element containing a quinoxaline compound which is
10 shown by the general formula (I). (In the formula, Z indicates a single bound, -O-, -SO₂-, -S-, -CH=CH-, -CO-, -NH-, and -N=N-; and X and Y respectively indicates hydrogen, an alkyl group having 1 to 6 carbon atoms, a substituted or unsubstituted aryl group having 6 to 18 carbon atoms, or a substituted or unsubstituted heterocyclic residue group having 3 to 12 carbon atoms. The substituent is a nitro group, an amino group, a cyano group, a hydroxyl group, a
15 carboxyl group, a methylthio group, an ethylthio group, a halogen group, an alkoxy group having 1 to 6 carbon atoms, an alkoxy carbonyl group having 1 to 6 carbon atoms, a dialkylamino group having 1 to 8 carbon atoms, a dialkyleneoxy group having 2 to 12 carbon

atoms, an alkyleneoxy group having 1 to 6 carbon atoms, an alkyleneoxy group having 1 to 6 carbon atoms, or an alkyl group having 1 to 6 carbon atoms. Also, "n" is an integer of 1 to 3.)

[Claim 2]

5 An organic electroluminescence element wherein a layer containing the quinoxaline compound described in claim 1 is interposed between a pair of electrodes.

[Claim 3]

An organic electroluminescence element wherein at least one layer of an electron injection layer contains the quinoxaline compound described in claim 1.

[Claim 4]

10 An organic electroluminescence element wherein at least one layer of a light emitting layer contains the quinoxaline compound described in claim 1.

[Claim 5]

An organic electroluminescence element wherein at least one hole injection layer contains the quinoxaline compound described in the claim 1.

15 [Detailed Description of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention is related to an organic electroluminescence element, more specifically to an organic electroluminescence element which achieves a high luminance, a high luminous 20 efficiency, and a longer lifetime by use of the quinoxaline compound as a constituent of the organic electroluminescence element.

[0002]

[Prior Art and Problems to be Solved by the Invention]

Efforts has been made for achieving a higher luminous efficiency by providing of an electron 25 injection layer to an organic electroluminescence element (hereinafter referred to as an "an organic EL element. In this case, there was a defect that exciplex formation was occurred and the lifetime of the light emission was short, though a light emission having a high luminance was able to be obtained. Also, it was necessary to prevent such a phenomenon that an organic layer was peeled away from a metal electrode by a long time electrical conduction, or an 30 organic layer and a metal electrode crystallize and become cloudy, which makes the luminance

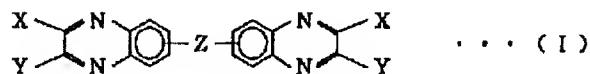
decrease. U.S. Patent No. 5,077,142 (1991) discloses 2,3-diphenylquinoxaline as an example of using the quinoxaline compound as a constituent of the organic EL. However, since a melting point was low such as 124 °C to 125 °C, there were some problems that the crystallization easily happened, and the light was hardly emitted. Thus, the present inventors 5 made efforts to overcome the forgoing problems.

[0003]

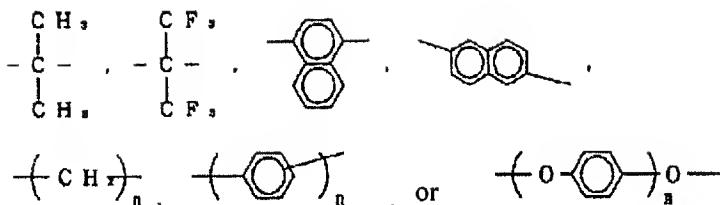
[Means for solving the Problem] As a result of their efforts, they have found a solving for the above problems by using the quinoxaline compound as a constituent of the organic EL element. The present invention was completed based on the findings of the above.

10 [0004-0008] That is, the present invention is related to the organic EL element which contains a quinoxaline compound shown by the general formula (I). (In the formula, Z indicates a single bound, -O-, -SO₂-, -S-, -CH=CH-, -CO-, -NH-, and -N=N-, and X and Y respectively indicates hydrogen, an alkyl group having 1 to 6 carbon atoms, a substituted or unsubstituted aryl group having 6 to 18 carbon atoms, or a substituted or a heterocyclic residue group having 3 to 12 15 carbon atoms. The substituents are a nitro group, an amino group, a cyano group, a hydroxyl group a carboxyl group, a methylthio group, an ethylthio group, a halogen group, an alkoxy group having 1 to 6 carbon atoms, an alkoxy carbonyl group having 1 to 6 carbon atoms, a dialkylamino group having 1 to 8 carbon atoms, a dialkyleneoxy group having 2 to 12 carbon atoms, an alkylene dioxy group having 1 to 6 carbon atoms, an alkyleneoxy group having 1 to 6 20 carbon atoms, or an alkyl group having 1 to 6 carbon atoms. Also, "n" is an integer of 1 to 3.)

[Chemical Formula 3]



[Chemical Formula 4]

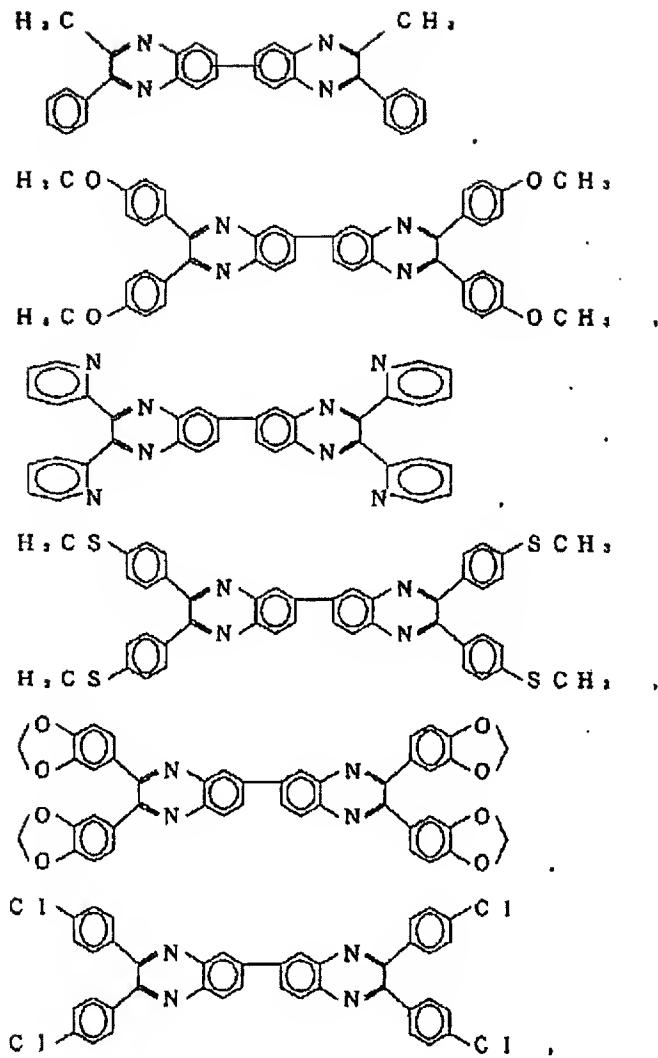


[0009] The present invention is related to an organic EL which contains a quinoxaline compound shown by the general formula (I). X and Y in the general formula (I) indicates an alkyl group having 1 to 6 carbon atoms such as hydrogen, a methyl group, an ethyl group, a 5 propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a tert-butyl group, a sec-butyl group, an isopentyl group, a tert-pentyl group, a neopentyl group, a hexyl group, an isohexyl group, and a cyclohexyl group, and an aryl group having 6 to 18 carbon atoms such as a substituted or unsubstituted phenyl group, a biphenyl group, a naphthyl group, an anthryl group, a terphenyl group, a pyrenyl group, and a heterocyclic residue group having 3 to 12 10 carbon atoms such as a substituted or unsubstituted furan group, a thiophene group, a pyrrole group, a pyrazole group, an imidazole group, a triazole group, an isooxazole group, an oxazole group, a frazan group, an isothiazole group, a thiazole group, a pyridine group, a pyrimidin group, a pyrazine group, an oxazine group, a thiazine group, a benzofuran group, a thionaphthene group, a benzoxazole group, a benzothiazole group, a quinoline group, an 15 isoquinoline group, a quinoxaline group, a quinazoline group, a phthalazine group, an acridine group, a phenazine group, a thianthren group. In these heterocyclic residue groups, preferably, at least either X or Y contains hetero atoms (N, S, O). An alkoxy group having 1 to 6 carbon atoms such as a nitro group, an amino group, a cyano group, a hydroxyl group, a carboxyl group, a methylthio group, an ethylthio group, halogen (fluorine, chlorine, iodine, bromine), a 20 methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, a n-butoxy group, an isobutoxy group, a tert-butoxy group, a sec-butoxy group, an isopentoxy group, a tert-pentoxyl group, a neopentoxyl group, a hexyloxy group, and an isohexyloxy group, an alkoxy carbonyl group having 1 to 6 carbon atoms such as a phenoxy carbonyl group, a methoxycarbonyl group, an ethoxycarbonyl group, a proxycarbonyl group, and a t-butoxycarbonyl group, a dialkylamino 25 group having 1 to 8 carbon atoms such as a dimethylamino group, a diethylamino group, a dipropylamino group, a diisopropylamino group, a di(n-butyl)amino group, an isobutylamino

group, a di(tert-butyl)amino group, and a di(sec-butyl) amino group, a dialkyleneoxy group having 2 to 12 carbon atoms such as a dimethylenoxy group, a diethylenoxy group, and a dipropylenoxy group, an alkyleneoxy group having 1 to 6 carbon atoms such as a methylenedioxy group, an ethylenedioxy group, and a propylenedioxy group, an alkyleneoxy group having 1 to 6 carbon atoms such as a methylenoxy group, an ethyleneoxy group, and a propyleneoxy group, and an alkyl group having 1 to 6 carbon atoms such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a tert-butyl group, a sec-butyl group, an isopentyl group, a tert-pentyl group, a neopentyl group, a hexyl group, and an isohexyl group are taken as examples of the substituted group. The X and Y 5 may be bonded between substituents to form a saturated or unsaturated 4 to 7-membered ring. Also, as for a quinoxaline compound which is used in the present invention, in the case where X and Y are different, structural isomers such as 6,6'-body, 6,7'-body, or 7,7'-body are generated by a bonding position of the quinoxaline ring at 6 and 7 position ; however, the quinoxaline may be formed of one or mixture of the above isomers. The quinoxaline 10 compound shown by the general formula (I) and used in the present invention is described below.

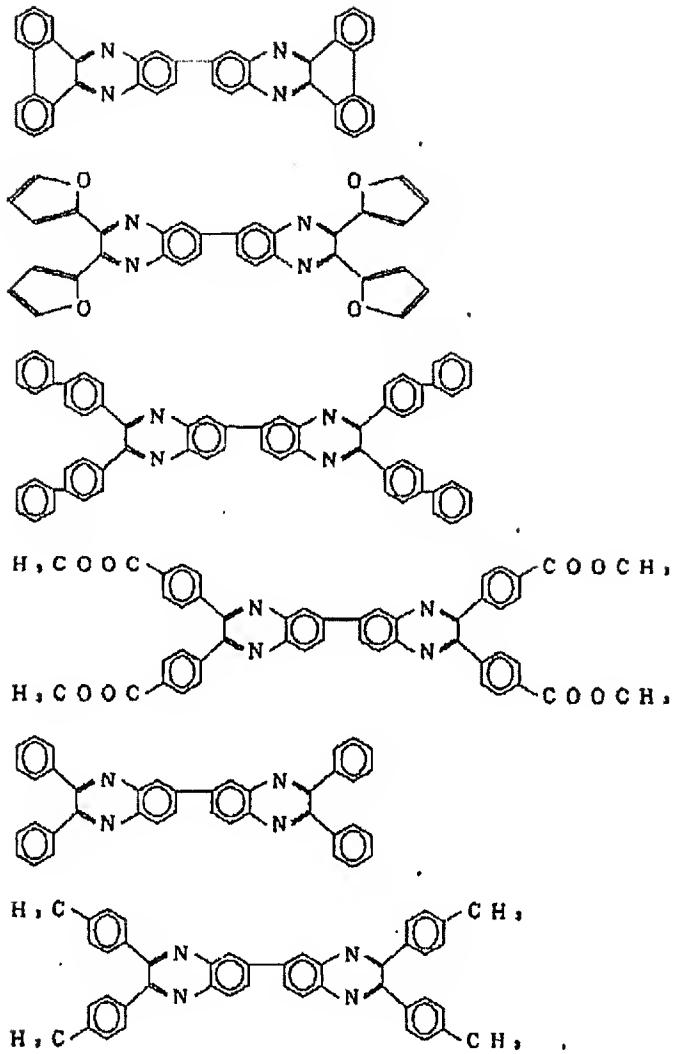
[0010]

[Chemical Formula 5]



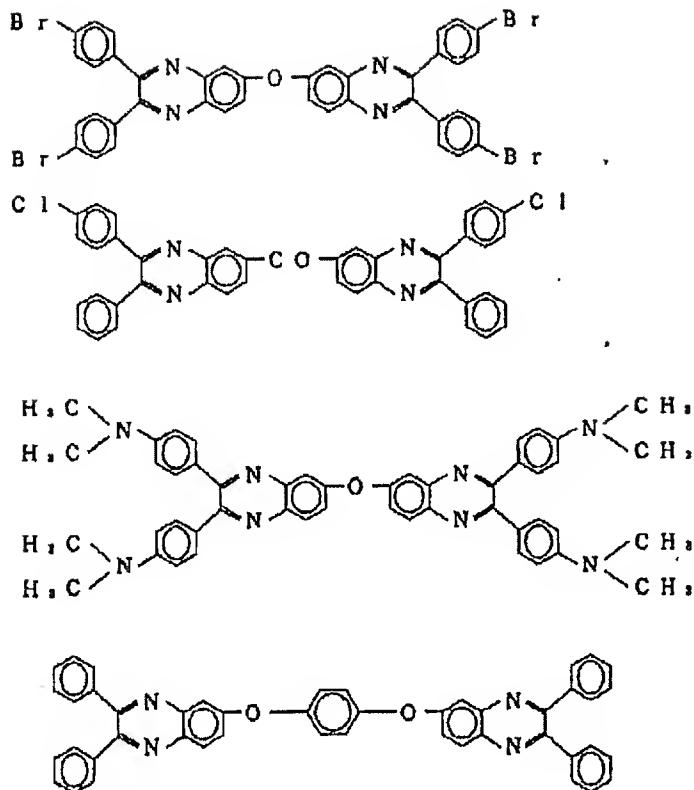
[0011]

[Chemical Formula 6]



[0012]

[Chemical Formula 7]



[0013] The present invention is related to the organic EL element which contains the quinoxaline compound, having a structure shown by the general formula (I). The types of structure such as anode/hole injection layer/light emitting layer/electron injection layer/cathode, 5 anode/light emitting layer/electron injection layer/cathode, anode/hole injection layer/light emitting layer/cathode, anode/light emitting layer/cathode, and the like are taken as examples of the organic EL element structure. The quinoxaline compound having a structure shown by the general formula (I) constitutes a part of a light emitting layer or an electron injection layer, preferably. As for the element structure, a hole injection layer or an electron injection layer is 10 not necessary, but the element having these layers has an advantage to increase a light emitting performance. Also, the mixture of the hole injection layer, light emitting layer, and electron injection layer may be interposed between a pair of the electrodes. In addition, the mixed layer may be made with use of the binder such as a high molecular compound in order to make each constituent stable.

[0014] Here, the organic EL element of the present invention is explained using an example of layers stacked by anode/hole injection layer/light emitting layer/electron injection layer/cathode. It is preferable to support an element of the present invention by a substrate. As for this substrate, there is no particular limitation as long as the substrate is made by commonly used 5 material for the conventional organic EL element, and for example, substrate made by a glass, transparent plastic, quartz, may be used.

[0015] It is preferable to use a metal, an alloy, an electro-conductive compound, and a mixture thereof having a high work function (4 eV or more) as a material for a positive electrode of this EL element. A metal such as Au, and a conductive transparent material such as CuI, ITO, 10 SnO₂, ZnO are given as a specific example for such an electrode material. The positive electrode can be made by formation of a thin film with a method such as evaporation or sputtering. In order to extract a light emission from this electrode, it is preferable to make the ratio of transmissivity more than 10%, and make a sheet resistance as the electrode several hundreds Ω/\square or less. Moreover, though depending on the material, the film thickness is 15 selected usually within the range of 10 nm to 1 μm , preferably, within the range of 10 nm to 20 nm.

[0016] On the other hand, a metal having a low work function (4 eV or less), an alloy, an electro-conductive compound, and a mixture thereof are used as a material for a negative electrode of this EL element. Sodium, sodium-cilium alloy, magnesium, lithium, 20 magnesium/copper mixture, magnesium/silver mixture, Al/Al₂O₃, indium and the like are taken as specific examples of such an electrode material. A thin film is formed by deposition of the electrode material with use of a method such as evaporation or sputtering, thus the cathode can be made. Also, it is preferable to make the sheet resistance several hundreds Ω/\square or less, and the film thickness is usually selected within the range of 10 to 500 nm, preferably 50 to 200 nm. 25 Note that in order to transmit the emitted light, it is more convenient if either anode or cathode of the organic EL element are transparent or semitransparent, the ratio of light emitting can increase effectively.

[0017] As a light emitting material for a light emitting layer of the present invention, it is preferable to use a quinoxaline compound having a structure shown by the above general 30 formula (I). In the case where this quinoxaline compound is used for elements other than the

light emitting layer; the light emitting material of the light emitting layer is not particularly limited, and any materials in the conventionally known compound can be used.

[0018] As a light emitting material other than the above quinoxaline compound, for example, compounds having a preferable thin film formation property such as a polycyclic condensed aromatic compound, a fluorescent bleach such as benzoxazole, benzothiazole, benzoimidazole, a metal chelated oxanoid compound, and a distilbenzene compound can be used. Here, a condensed ring light emitting substance and the like, including anthracene, naphthalene, phenanthrene, pylene, chrysene, perylene skeleton, are taken as examples of the polycyclic condensed aromatic compound.

10 [0019] As the fluorescent bleach such as the above benzoxazoles, benzothiazoles, benzoimidazoles, materials given in the Japanese Published Patent Application No. S59-194393 can be used. The benzoxazoles such as 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)-1,3,4-thiadiazole; 4,4'-bis(5,7-t-pentyl-2-benzoxazolyl)stilbene; 15 4,4'-bis(5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl)stilbene; 2,5-bis(5,7-di-t-pentyl-2-benzoxazole)thiophene; 2,5-bis(5-(α , α -dimethylbenzyl)-2-benzoxazolyl)thiophene; 2,5-bis(5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl)-3,4-diphenylthiophene; 20 2,5-bis(5-methyl-2-benzoxazolyl)thiophene; 4,4'-bis(2-benzoxazolyl)biphenyl; 5-methyl-2-(2-(4-(5-methyl-2-benzoxazolyl)phenyl)vinyl)benzoxazole; 2-(2-(4-chlorophenyl)vinyl)naphtho(1,2-d)oxazole and the like, benzothiazoles such as 2,2'-(p-phenylenedivinylene)-bisbenzothiazole, and the like, benzoimidazoles such as 2-(2-(4-(2-benzoimidazolyl)phenyl)vinyl)benzoimidazole; 2-(2-(4-carboxyphenyl)vinyl)benzoimidazole, and the like are taken as typical examples of such 25 a fluorescent bleach.

[0020] As for the above metal chelated compound, for example, materials given in the Japanese Published Patent Application No. S63-295695 can be used. As for a typical example for such a metal chelated oxide compound, 8-hydroxyquinolines metal hormogone, and the like such as tris(8-quinolinol)aluminum, bis(8-quinolinol)magnesium, bis(benzo(f)-8-quinolinol)zinc, 30 bis(2-methyl-8-quinolinolato)aluminumoxide, tris(8-quinolinol)indium,

tris(5-methyl-8-quinolinol)aluminum, 8-quinolinollithium, tris(5-chloro-8-quinolinol)gallium, bis(5-chloro-8-quinolinol)calcium, poly(zinc(II)-bis(8-hydroxy-5-quinolinonyl)methane), or a dilithiumepinetridione and the like are given.

[0021] Others such as a distilbenzene derivative in the specification of the Europatent No. 0373582, a dimethylden derivative in the specification of the Europatent No. 0388768, a coumarin derivative in Japanese Published Patent Application No. H2-19694, a distilpyrazine derivative in Japanese Published Patent Application No. H2-252793, a perylene derivative in Japanese Published Patent Application No. H2-196885, a naphthalene derivative Japanese Published Patent Application No. H2-255789, a phthaloperyamine derivative in Japanese Published Patent Application No. H2-289676 and Japanese Published Patent Application No. H2-88689, a styrylamine derivative in Japanese Published Patent Application No. H2-250292, cyclopentadiene derivative in Japanese Published Patent Application No. H2-289675 and the like are selected depending on objective emission color and performance as appropriate. The light emitting layer formed by the above organic compound may have a stacked structure of two or more layers as desired, and may be formed with fluorescent materials disclosed in U.S. Patent No. 4,769,292. In this case, the organic compound forms thin film layers and has a part of an injection function and a light emitting function at the light emitting region. On the other hand, a very small amount of the fluorescent materials (less than a few mol %) can exist in the organic compound layer and has a part of the light emitting function of emitting in response to the recombination of the electrons and holes. Additionally, a compound with no thin film property may be used as an organic compound at the light emitting region. As an example for such a compound, 1,4-diphenyl-1,3-butadiene; 1,1,4,4-tetraphenyl-1,3-butadiene; tetraphenylcyclopentadiene are taken. However, these materials with no thin film property have a disadvantage of a short lifetime of the element. This light emitting layer may be structured by single layer formed by one or plural kinds of the light emitting materials, or may be stacked by a compound other than the above light emitting layer.

[0022] Then, a hole injection layer of the organic EL is made of a hole transferring compound and has a function to transfer a hole which is injected by an anode electrode to a light emitting layer. By interposing this hole injection layer between anode and light emitting layer, more holes are injected into the light emitting layer with a lower electric field. Also, an electron

which is injected into the light emitting layer from cathode or electron injection layer is accumulated on the interface of the light emitting layer by a barrier of an electron existing on the interface of the light emitting layer and hole injection layer, and becomes an element having an excellent characteristic of a light emitting efficiency. A hole transferring compound used 5 for such a hole injection layer may transfer a hole to the light emitting layer appropriately in the case where it is provided between two electrodes having a light-emitting field and where a hole is injected from anode. For example, it is preferable to have a hole mobility of at least 10^{-6} cm²/V·sec when an electric field of 10^4 - 10^6 V/cm is applied. This hole transferring compound is not limited as long as having the preferable characteristics. It can be selected from a 10 compound which is generally used as an electron injection transporting material of a hole for a photo conductive material, or the known compound which is used for a hole injection layer of the EL element.

[0023] As for the hole transmission compound, a quinoxaline compound shown by the general formula (I), a triazole derivative, an oxazole derivative (such as described in the U.S. Patent No. 15 3,189,447), an imidazole derivative, a polyarylalkane derivative, a pirazoline derivative, a pirazolone derivative, a phenylenediamine derivative, an arylamine derivative, an amino-substituted chalcone derivative, an oxazole derivative, a stilanthracene derivative, a fluorenone derivative, a hydrazone derivative, a stilbene derivative, and the like are taken as examples. Also, as for a charge injection transporting material, a silazane derivative, 20 polysilane, aniline copolymer, and conductive high molecular oligomer, especially for thiophenoligomer, and the like are taken as examples.

[0024] In the present invention, the hole transmission compound or a charge injection transporting material can be used as a hole injection material, and it is preferable to use the following materials: a porphyrin compound (such as given in the Japanese Published Patent 25 Application No. S63-2956965) and an aromatic tertiary amine compound and a styrylamine compound (refer to the specification of the U.S. Patent No. 4,127,412, Japanese Published Patent Application Nos. S53-27033, S54-58445, S54-149634, S54-64299, S55-79450, S55-144250, S56-119132, S61-295558, S61-98353, S63-295695 and the like); specifically, an aromatic tertiary amine is preferably used. As typical examples of the porphyrine compound, 30 porphyrine, 1,10,15,20-tetraphenyl-21H,23H-porphinecopper(II);

1,10,15,20-tetraphenyl-21H,23H-porphinezinc(II);

5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphine; siliconephthalocyanineoxide;

aluminumphthalocyaninechloride; phthalocyanine (nonmetal); dilithium phthalocyanine; copper
tetramethylphthalocyanine; copper phthalocyanine; chromiumphthalocyanine; zinc phthalocyanine;

5 lead phthalocyanine; thitanium phthalocyanine oxide; magnesium phthalocyanine; copper
octamethylphthalocyanine and the like are provided.

[0025] Also, as typical examples of an aromatic tertiary amine compound and a styrylamine
compound,

N,N,N',N'-tetraphenyl-4,4'-diaminophenyl;

N,N'-diphenyl-N,N'-di(3-methylphenyl)-4,4'-diaminobiphenyl (TPDA); 2,2-bis

10 (4-di-p-tolyaminophenyl)ptopane; 1,1,-bis(4-di-p-tolyaminophenyl)cyclohexane;

N,N,N',N'-tetra-p-tolyl-4,4'-diaminobiphenyl;

1,1-bis(4-di-p-tolyaminophenyl)-4-phenylcyclohexane;

bis(4-di-p-dimethylamino-2-methylphenyl)phenylmethane;

bis(4-di-p-tolyaminophenyl)phenylmethan;

15 N,N'-diphenyl-N,N'-di(4-methoxyphenyl)-4,4'-diaminobiphenyl;

N,N,N',N'-tetraphenyl-4,4'-diaminophenylether; 4,4'-bis(diphenylamino)quadriphenyl;

N,N,N-tri(p-tolyl)amine; 4-(di-p-tolylamino)-4'-[4(di-p-tolylamino)stylyl]styrylben;

4-N,N-diphenylamino-(2-diphenylvinyl)benzene;

3-methoxy-4'-N,N-diphenylaminostyrylbenzene; N-phenylcarbazole and the like are provided.

20 Also, crystalline or non-crystalline materials of inorganic semiconductor, such as Si, SiC and
CdS can be used. This hole injection layer may be stacked by a single layer which is
structured by either one kind or plural kinds of the hole injection materials, or may be stacked
by the hole injection layer which is structured by a different kind of compound.

[0026] Also, the electron injection layer of the organic EL element used in the present invention
25 is structured by the electron injection material and has a function to transport an electron which
is injected from the cathode to the light emitting layer. In the case of the present invention, it
is preferable to use a compound shown by the general formula (I). In the case where this
quinoxaline compound is used for the element other than the electron injection layer, the
electron injection material is not specifically limited, and conventionally known compounds are
30 used and selected.

[0027] This electron injection layer may be stacked by a single layer which is structure by one or plural kinds of these electron injection materials, or may be stacked by an electron injection layer which is structured by a different kind of compound. Also, a hole injection material which is made by p-type Si or p-type SiC or an electron injection material which is made by 5 n-type α -Si or n-type α -SiC, which is an inorganic material, may be used as an electron injection material. An inorganic semiconductor disclosed in the WO 90/05998 is provided as an example.

[0028] Then, as for the method of the present invention, a preferable example of manufacturing the organic EL is explained. For example, manufacturing method of the EL element which has 10 anode/hole injection layer/light emitting layer/electron injection layer/cathode is explained below. A desired electrode material such as a thin film formed by an anode material is formed over an appropriate substrate of which film thickness is less than 1 μ m, preferably, within the range of 10 to 200 nm, by a method such as evaporation or sputtering, and an anode is manufactured. Then, a thin film is formed by a hole injection layer, a light emitting layer, an 15 electron injection layer which are element materials. As for the method of forming the thin film, the above spin coating method, cast method, evaporation method can be used. Especially, a vacuum evaporation method is preferably used since a uniform film thickness is likely to be obtained and a pin hole is unlikely to be generated. In the case where this evaporation method is used for the thin film formation, the evaporation condition is different depending on kinds of 20 compounds, a crystal structure for the target molecular deposited film, an assembling structure, and the like, but it is preferable to select the board heat temperature within the range of 50 to 400 $^{\circ}$ C, the degree of vacuum within 10^{-6} to 10^{-3} Pa, the evaporation rate within 0.01 to 50 nm/sec, substrate temperature within -50 to 300 $^{\circ}$ C, and film thickness within the range of 5nm to 5 μ m as appropriate. After the formation of these layers, a thin film formed by cathode 25 materials is formed over these layers to have a film thickness less than 1 μ m, preferably within the range of 50 to 200nm, by providing the cathode by a method such as evaporation or sputtering, whereby, the desired EL element is obtained. Note that it is possible to reverse the formation order, and the organic EL element may be formed in the order of: an electron injection layer, a light emitting layer, a hole injection layer, and anode. Also, as for the 30 manufacturing method of an element which is formed by anode/light emitting layer/cathode and

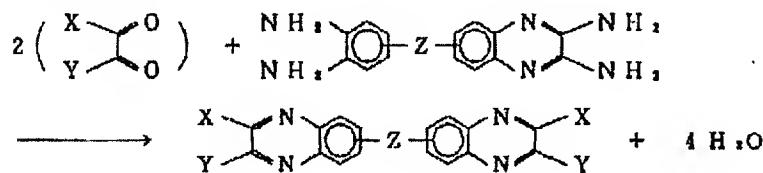
interposed between a pair of electrodes in the state of mixing the hole injection layer, the light emitting layer and the electron injection layer; for example, a thin film made of a material for anode is formed over an appropriate substrate, a solvent which is made of a hole injection material, a light emitting material, an electron injection material, tying agent such as 5 polyvinylcarbazole, polycarbonate, polyarylate, polyester, or polyethel, and the like is applied. Alternatively, a method that a thin film is formed from the solvent with use of an immersion coating method to be a light emitting layer; then, another thin film made of a material for a cathode is formed thereover is given. An element material which is a material for a light emitting layer or an electron injection layer may be evaporated in vacuum over the 10 manufactured light emitting layer, and a thin film made of a material for cathode may be formed thereover.

[0029] When a DC voltage of 5 to 40 V is applied to the organic EL element which was thus obtained, light emission can be observed in the case of setting the anode to plus polarity, and the cathode to minus polarity. Here, when the voltage is applied in the case where the polarity 15 of the anode and cathode are opposite; the current dose not flows and light emission does not occur. Further, when an alternating voltage is applied, a uniform light emission can be observed only when anode has plus polarity, and cathode has minus polarity. Any wave form of the alternating voltage to be applied is acceptable.

[0030] Here, a synthetic method of a quinoxaline compound shown by the general formula (I) 20 which is one of the features of the present invention will be briefly mentioned. Note that the synthesis method of the quinoxaline compound used in the present invention is not limited to the methods below. The synthetic method of the quinoxaline compound is subject to the following synthetic scheme.

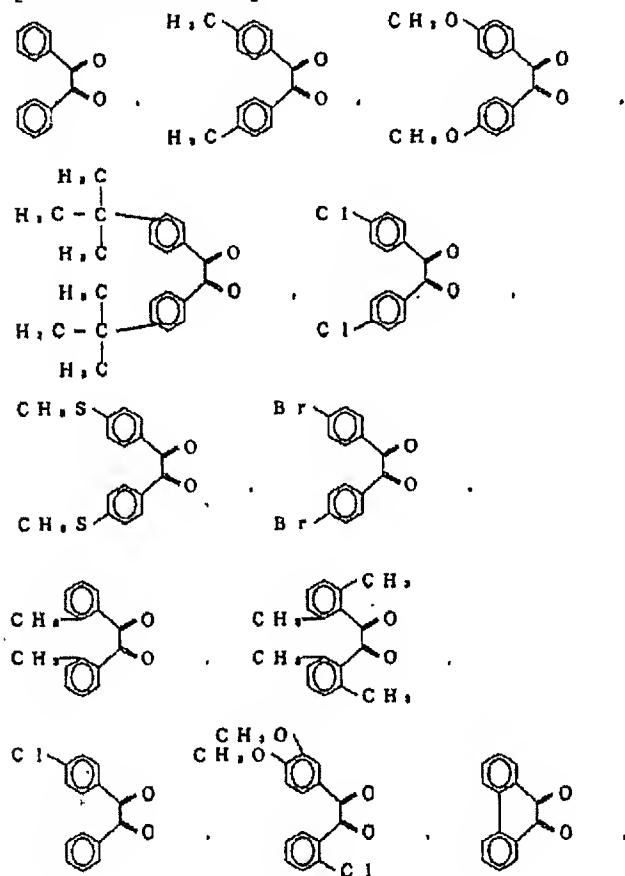
[0031]

[Chemical Formula 8]

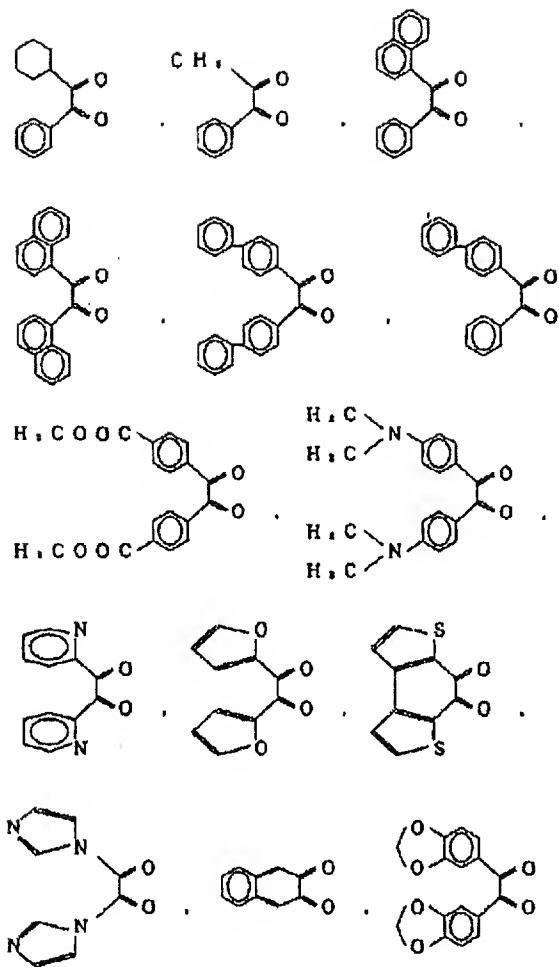


[0032-37] Specifically, α -diketone and o-phenylenediamine derivative is heated and stirred in a solvent such as chloroform, alcohol (methanol, ethanol, propanol, butanol, amylalcohol or the like), or ethyl acetate, or heated and stirred at around 200 °C in a non-solvent. A reaction time is preferably 0.1 to 20 hours. In the case where X and Y are different, a mixed structural 5 isomer such as 6,6'-body, 6, 7'-body, or 7,7'-body is generated by the bonding position of the quinoxaline ring. As for diketone to be used here, the following compounds can be given. Also, as for an o-phenylenediamine derivative, the following compounds can be given.

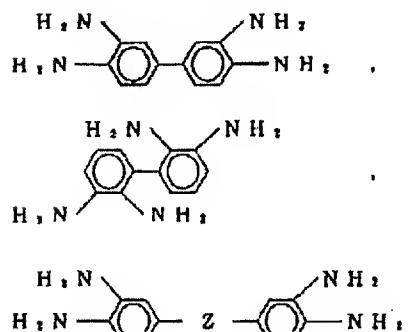
[Chemical Formula 9]



[Chemical Formula 10]



[Chemical Formula 11]



(In the formula, Z is the same as the aforementioned.)

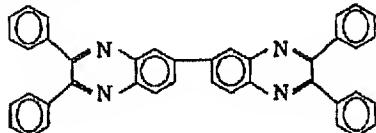
[0038]

[Example] The present invention is explained in details with synthetic examples, examples, and comparative examples.

5 Synthetic Example 1

[0039]

[Chemical Formula 12]



[0040] Synthesis of 2,2',3,3'-tetraphenyl-6,6'-diquinoxaline

2.14g (0.01 mol) of 3, 3' -diaminobenzine and 4.2 g (0.02 mol) of benzyle were refluxed in
10 chloroform for eight hours and the solvent is filtered, whereby an ocher powder was obtained. Also, 5.0g (yield: 89 % (0.0089 mol) of a light yellow powder was obtained by reprecipitating the ocher powder with toluene. A melting point of the light yellow powder was 312 °C. As for a result of mass spectrometry of the light yellow powder, $m/Z = 562 (M^+)$. Also, a result of a proton nuclear magnetic resonance measurement (1H -NMR, standard: tetramethylsilane
15 (TMS), solvent: dimethylsulfoxide (DMSO), measured wavelengths: 400 MHz) is as follows:

$\delta = 7.35$ to 7.44 ppm (m, 12H, H at 3, 4-position of a phenyl group),
 $\delta = 7.52$ to 7.57 ppm (m, 8H, H at 2-position of a phenyl group),
 $\delta = 8.3$ ppm (d, 2H, H at 8-position of a quinoxaline group),
 $\delta = 8.45$ ppm (q, 2H, H at 7-position of a quinoxaline group), and
20 $\delta = 8.54$ ppm (d, 2H, H at 5-position of a quinoxaline group).

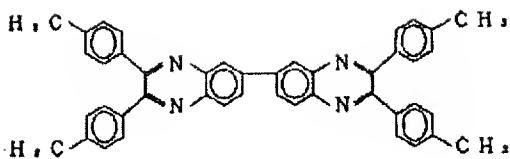
From the above result, it was confirmed that the aimed quinoxaline compound was synthesized.

Note that in the example, with use of methylene chloride as a developing solvent, a purified substance separated from the above light yellow powder by silica gel column was used.

[0041] Synthetic Example 2

25 [0042]

[Chemical Formula 13]



[0043] Synthesis of 2,2',3,3'-tetra(p-tolyl)-6,6'-diquinoxaline

2.14g (0.01mol) of 3,3'-diaminobenzyn was dissolved into mixed solution of n-butanol of 40 mL and acetic acid of 20 mL; and a warm solution containing 4.8g (0.02 mol) of 5 4,4'-dimethylbenzyl was added into 20 mL of acetic acid; and the mixed solution was stirred at 80°C for four hours. After cooling down the solution, a generated ocher powder was subject to suction filtration. 5.0g (yield: 95% (0.0095 mol) of a light brown powder was obtained by washing this ocher powder with cooled ethanol. A melting point of this yellow powder was 334 °C. As a result of mass spectrometry of the obtained light brown powder, $m/Z=618 (M^+)$.

10 Also, results of measurement by the proton nuclear magnetic resonance (1H -NMR, standard: TMS, solvent: DMSO, measured wavelengths: 400MHz) are as follows:

$\delta = 2.35$ ppm (s, 12H, H at 3-position of phenyl),

$\delta = 6.92$ to 6.98 ppm (m, 8H, H at 3-position of phenyl),

$\delta = 7.46$ to 7.53 ppm (m, 8H, H at 2-position of phenyl),

15 $\delta = 8.22$ ppm (d, 2H, H at 8-position of quinoxaline ring),

$\delta = 8.37$ ppm (q, 2H, H at 7-position of quinoxaline ring), and

$\delta = 8.55$ ppm (d, 2H, H at 5-position of quinoxaline ring).

From the above result, it was confirmed that the aimed quinoxaline compound was synthesized.

Note that in the example, with use of methylene chloride as a developing solvent, a purified

20 substance separated from the above light yellow powder by silica gel column was used.

[0044] Synthetic Example 3 to 17

The reaction was performed in the same manner as that in the Synthetic Example 1 except that the diketone and the tetra amino aromatic compound shown in the Table 1 were used. The obtained quinoxaline compound is provided in Table 2. Note that the compounds of the

25 Synthetic Examples 7, 8, 9 and 12 are purified by a sublimate method.

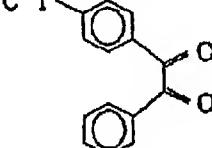
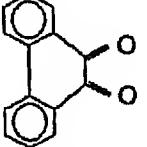
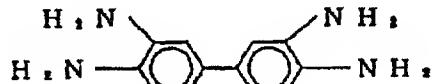
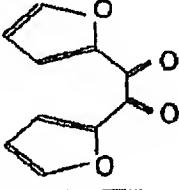
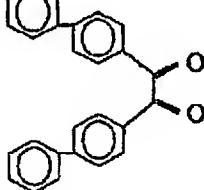
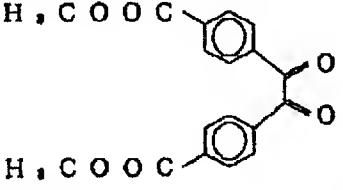
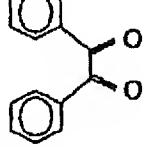
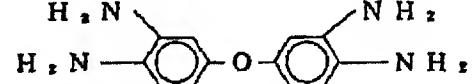
[0045] [Table 1]

First Table (1)

	Diketone compound	Tetra amino aromatic compound
Synthetic Example 3		
Synthetic Example 4		
Synthetic Example 5		
Synthetic Example 6		
Synthetic Example 7		

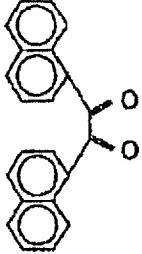
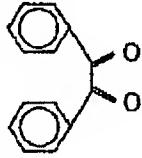
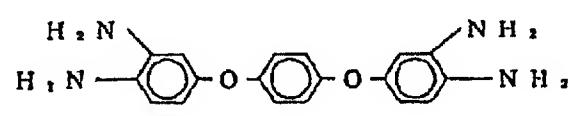
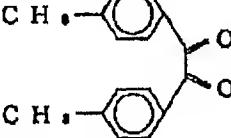
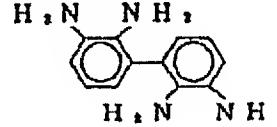
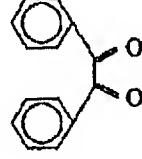
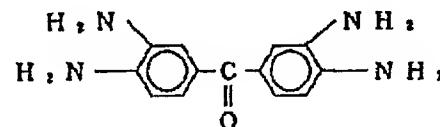
[0046]

First Table (2)

	Diketone compound	Tetra amino aromatic compound
Synthetic Example 8		
Synthetic Example 9		
Synthetic Example 10		
Synthetic Example 11		
Synthetic Example 12		
Synthetic Example 13		

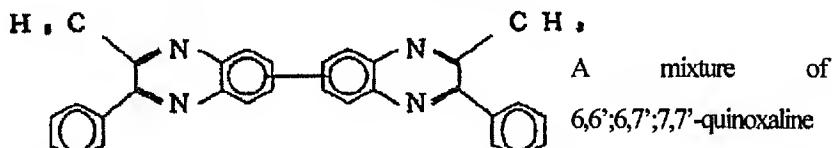
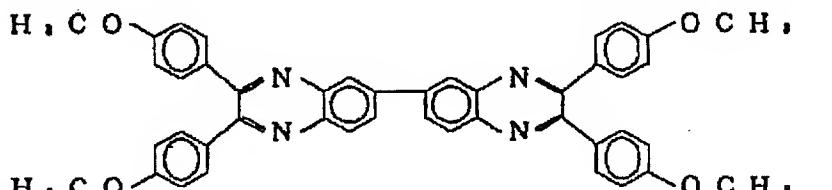
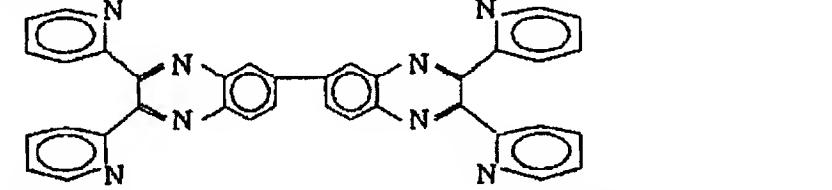
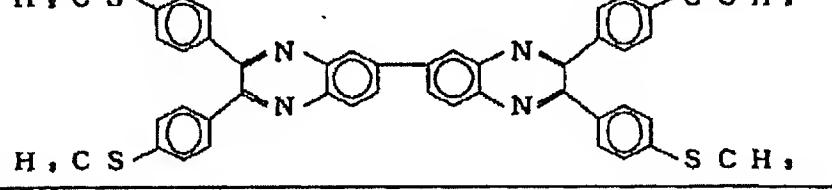
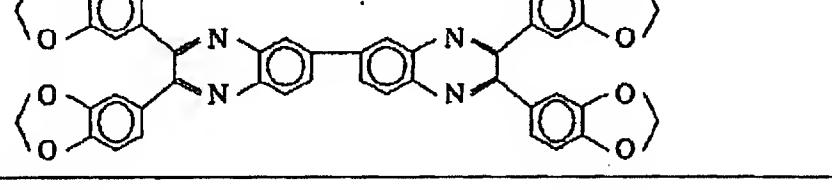
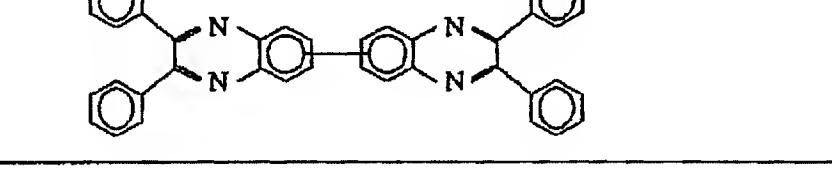
[0047] Table 3

First Table (3)

	Diketone compound	Tetra amino aromatic compound
Synthetic Example 14		
Synthetic Example 15		
Synthetic Example 16		
Synthetic Example 17		

[0048] Table 4

Second Table (1)

	Quinoxaline Compound
Synthetic Example 3	
Synthetic Example 4	
Synthetic Example 5	
Synthetic Example 6	
Synthetic Example 7	
Synthetic Example 8	

[0049] Table 5

Second Table (2)

	Quinoxaline compound
Synthetic Example 9	
Synthetic Example 10	
Synthetic Example 11	
Synthetic Example 12	
Synthetic Example 13	

[0050] Table 6

Second Table (3)

Quinoxaline compound	
Synthetic Example 14	
Synthetic Example 15	
Synthetic Example 16	
Synthetic Example 17	

[0051] Example 1

A glass substrate on which an ITO transparent electrode of 100 nm film thickness (25mm × 75mm × 1.1mm: manufactured by HOYA Corporation) was used as a transparent supporting substrate. This substrate was subjected to ultrasonic cleaning with isopropyl alcohol for 30 minutes, further soaked and washed. This transparent supporting substrate was dried with drying nitrogen gas, and fixed to a substrate holder of a commercial vacuum evaporation device.

On the other hand, N,N' -diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPDA) of 200 mg was put in a molybdenum resistance heating boat, and 2,2',3,3'-tetraphenyl-6,6'-diquinoxaline (TPDQ) of 200mg was put in another molybdenum resistance heating boat and fixed to the vacuum evaporation device. First, after the pressure of 5 a vacuum layer was reduced to 4×10^{-4} Pa, a current was supplied to the heating boat in which TPDA was put, and the boat was heated up to 200 °C. The vacuum chamber was evaporated over a transparent supporting substrate at an evaporation rate of 0.1 to 0.3 nm/sec and a hole injection layer of 60 nm film thickness was formed. Then a current was supplied to the heating boat in which DPVBi was put and the boat was heated up to 220 °C. DPVBi was 10 evaporated over the hole injection layer at an evaporation rate of 0.1 to 0.3 nm/sec and a light emitting layer of 40 nm film thickness was formed. Furthermore, a current was applied to the heating boat in which TPDQ was put and the boat was heated up to 314 °C. Then TPDQ was evaporated over the light emitting layer at the evaporation rate of 0.1 nm/sec and an electron injection layer of 20 nm thicknesses was formed. Note that the substrate temperature at the 15 time of evaporation was at a room temperature. Then, a vacuum layer was opened, and a mask made of stainless steel was provided over an electron injection layer. On the other hand, magnesium of 3 g was put in the molybdenum heating boat, and silver of 0.5 g was put in the tungsten basket for evaporation. After the pressure in the vacuum layer was reduced to 2×10^{-4} Pa, a current was applied to the boat in which magnesium was put and magnesium was 20 evaporated at the evaporation rate 1.5 to 2.0 nm/sec. At the same time, the basket in which silver was put was heated and silver was evaporated at the evaporation rate of 0.1 nm/sec, thus a counter electrode made of the mixture of magnesium and silver; whereby, the target organic EL was made. When a DC voltage of 10 V was applied to the ITO electrode of this element serving as an anode, and applied to the counter electrode made of the mixture of magnesium 25 and silver serving as a cathode, a current density of 14 mA/cm² follows and a blue light was obtained. The maximum wave length of this emitted light was 474 nm, luminous was 230 cd/m², and luminous efficiency was 0.52 lumen/W. Even 50 hours later after applying a current, the surface of the electrode was not peeled away or did not become cloudy. The blue light was able to be recognized.

30 [0052] Examples 2 to 13

English Translation of JP H6-207169

Except that the compounds provided in the Third Table was used instead of TPDQ and heating temperature at the time of evaporation was changed as shown in the Third Table, an element was manufactured and evaluated in the same manner as in the Example 1. The obtained result is shown in the Third Table.

5 [0053] [Table 7]

Third Table

	Quinoxaline compound	Evaporation boat temperature (°C)	Applied voltage (V)	Current density (mA/cm ²)	Luminance (cd/m ²)
Example 2	Synthetic Example 2	320	10	59	930
Example 3	Synthetic Example 3	245	10	9	93
Example 4	Synthetic Example 4	333	10	104	490
Example 5	Synthetic Example 5	345	10	70	375
Example 6	Synthetic Example 6	333	10	12	128
Example 7	Synthetic Example 7	318	10	13	120
Example 8	Synthetic Example 8	300	10	23	140
Example 9	Synthetic Example 9	325	10	41	212
Example 10	Synthetic Example 10	295	10	18	135
Example 11	Synthetic Example 11	393	10	24	212
Example 12	Synthetic Example 12	310	10	19	144
Example 13	Synthetic Example 13	297	12	19	180

[0054] [Table 8]

Third Table (continued)

	Luminous efficiency (lumen/W)	Peak wavelength of the emission spectrum (nm)	Adhesiveness of electrodes	Lifetime of elements (hour)
Example 2	0.53	474	preferable	More than 50 hours

Example 3	0.32	482	preferable	More than 50 hours
Example 4	0.15	483	preferable	More than 50 hours
Example 5	0.17	484	preferable	More than 50 hours
Example 6	0.33	483	preferable	More than 50 hours
Example 7	0.29	480	preferable	More than 25 hours
Example 8	0.19	478	preferable	More than 25 hours
Example 9	0.16	481	preferable	More than 25 hours
Example 10	0.24	474	preferable	More than 25 hours
Example 11	0.28	475	preferable	More than 25 hours
Example 12	0.20	474	preferable	More than 25 hours
Example 13	0.25	473	preferable	More than 50 hours

[0055] Example 14

Except that a tris(8-hydroxyquinoline)aluminum was used instead of DPVBi and heating boat temperature at the time of evaporation was changed to 280 °C, an element was manufactured 5 and evaluated in the same manner as the Example 1. When a DC voltage of 10 V is applied to the ITO electrode serving as an anode and the counter electrode which is made of a mixture of magnesium and silver serving as a cathode, a current of which density is 48mA/cm² flows and green light is obtained. The maximum wavelength of this emitted light was 510 nm, the luminous was 670 cd/m², and the luminous efficiency was 0.44 lumen/W. Even 50 hours later 10 after applying a current, the surface of the electrode was not peeled away, and did not become cloudy even 50 hours later. The green light emission was still recognized.

[0056] Example 15

Except that TPDQ was used instead of DPVBi and heating boat temperature at the time of evaporation was changed into 314 °C, the pressure in the vacuum chamber was reduced to 4 × 15 10⁻⁴ Pa in the same manner as the Example 1. After that, 60 nm film thickness TPDQ was formed in the same manner as the Example 1 and a boat in which TPDQ was put was heated up to 314 °C and a layer was stacked to have a thickness of 60 nm at the evaporation rate of 0.1nm/sec. Note that the substrate temperature at the time of evaporation was at a room temperature. After the vacuum chamber was opened and a mask was provided over the

evaporated material, a counter electrode made of the mixture of magnesium and silver was stacked by evaporation, and the aimed elements were manufactured and evaluated in the same manner as the Example 1. When a DC voltage of 15V was applied while ITO electrode of this element serves as anode and the counter electrode made of a mixture of magnesium and silver 5 serves as cathode, a current of which density is 14 mA/cm² flows, and violet-blue light is obtained. The maximum wavelength of this emitted light was 450 nm, the luminance is 200 cd/m², and the luminous efficiency was 0.3 lumen/W. Even 50 hours later after applying a current, the surface of the electrode is not peeled away, and does not cloudy. The violet-blue light emission was still recognized.

10 [0057] Example 16

A glass substrate (25 mm × 75 mm × 1.1 mm: manufactured by HOYA Corporation) having an ITO transparent electrode of which film thickness was 100 nm was used as a transparent supporting substrate. This transparent supporting substrate was washed by ultrasonic cleaning with isopropyl alcohol for 30 minutes, and further soaked and washed. Then, this supporting 15 substrate was dried with a dry nitrogen gas and fixed on a substrate holder of a commercial vacuum evaporation device. On the other hand, a solution which was given by dissolving TPDA of 200 mg and poly(N-vinylcarbazole) of 200mg in a chlorobenzene of 40ml was deposited on a resistance heating board made of molybdenum with use of spin coating, and a hole injection layer was made. Additionally, a solution which was obtained by dissolving 20 DPVBi of 200 mg and 2,2',3,3'-tetra(p-tolyl)-6,6'-diquinoxaline of 200 mg obtained in the Synthetic Example 2 into chloroform of 20g was deposited with use of spin coating, and a light emitting layer was obtained. The spin-coating was conducted at a rate of 7000 rotation/min. for 50 seconds, and the film thickness was 500 ± 100 Å. Then, the obtained substrate was fixed on a substrate holder of the vacuum evaporation device, and magnesium of 3g was put 25 into the resistance heating boat which was made of molybdenum. Also, after an indium of 1g was put into another resistance heating boat which was made of molybdenum, and the voltage of the vacuum layer was reduced to 4×10^{-4} Pa again, a current was flowed to the boat containing magnesium and the magnesium was evaporated at the evaporation rate of 2 to 3 nm/sec. At the same time, the indium in another boat which was made of molybdenum was 30 heated and evaporated at the evaporation rate of 0.1 to 0.2 nm/sec. As a result, the aimed

organic EL element was made with use of a mixture of magnesium and indium as a counter electrode. When a DC voltage of 12 V was applied to the ITO electrode of this element serving as an anode and the counter electrode which was made of a mixture of magnesium and silver serving as a cathode, a current of which density was 58 mA/cm^2 flows, and green-blue light was obtained. The highest wavelength of this light was 480nm, luminous was 320 cd/m^2 , and the luminous efficiency was 0.14 lumen/W. Even 50 hours later after applying a current, the surface of the electrode was not peeled away and did not become cloudy even 50 hours later after. The green-blue light was still obtained.

[0058] Examples 17 to 20

10 Except that the compounds provided in the Fourth Table were used instead of TPDQ and heating temperature at the time of evaporation was changed as shown in the Fourth Table; an element was made and evaluated in the same manner as the Example 1. The obtained result is shown in the Fourth Table.

[0059] Table 9

15

Fourth Table

	Quinoxaline compound	Evaporation boat temperature (°C)	Applied voltage (V)	Current density (mA/cm ²)	Luminous (cd/m ²)
Example 17	Synthetic Example 14	300	12.5	14	221
Example 18	Synthetic Example 15	340	12	16	169
Example 19	Synthetic Example 16	190	11	9.1	110
Example 20	Synthetic Example 17	286	10	24	88

[0060] Table 10

Fourth Table (continued)

	Luminous efficiency (lumen/W)	Peak wavelength of the emission spectrum (nm)	Adhesiveness of electrodes	Lifetime of the elements (hour)
Example 17	0.40	476	Preferable	More than 25 hours

Example 18	0.28	470	Preferable	More than 25 hours
Example 19	0.35	470	Preferable	More than 50 hours
Example 20	0.12	480	Preferable	More than 25 hours

[0061] Comparative Example 1

Except that a sample which was purified by silica gel column using the methylene chloride as developing solution is used instead of TPDQ, and heating boat temperature at the evaporation 5 was changed to 215 °C; an element was manufactured and evaluated in the same manner as that in the Example 1. When a DC voltage of 14 V was applied to the ITO electrode of this element serving as an anode and the counter electrode which is made of a mixture of magnesium and silver serving as a cathode, a current of which density is 22 mA/cm² flows, and green-blue light is obtained. The maximum wavelength of this light was 484 nm, luminous 10 was 53 cd/m², and a luminous efficiency was 0.05 lumen/W. It was recognized that the surface of the electrode was peeled after application of a current. Also, the light emission attenuated significantly and the quenching of light occurred 0.5 hours later.

[0062]

[Effect of the present invention]

15 As described above, the organic EL element of the present invention has characteristics of a high luminance, a high light luminous efficiency, and long lifetime. Thus, the organic EL element of the present invention can be efficiently utilized in the chemical industry such as electronics, a display element, and the like.